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PASSIVATION OF ALUMINUM

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| <small>SUMMARY</small> Treatment of aluminum in a $\text{CrO}_3\text{-H}_3\text{PO}_4$ stripping solution and subsequently in a solution containing chromate, phosphate, and silicate at pH 5 deposits a passive film which resists attack by boiling water for more than 17 hours and has considerable resistance to abrasion | | <small>NO. PAGES</small> 2 |
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PASSIVATION OF ALUMINUM

D. A. Vermilyea and D. R. Ochar*

INTRODUCTION

Recent studies^(1, 2) have shown that the aluminum-water reaction proceeds by formation and dissolution of an amorphous oxide film. At low or high pH the products are soluble species, while at intermediate pH a layer of porous pseudoboehmite is formed on top of the amorphous oxide. This porous hydroxide layer provides deposition sites close to the surface for soluble species and hence allows a rapid reaction despite the very low solubility of aluminum hydroxide at neutral pH. Inhibition⁽²⁾ of the reaction in the pH range 4-7 is effected by certain inorganic ions which prevent the formation of the hydroxide layer and hence eliminate the deposition sites for soluble species.

This report concerns the passivation of aluminum by the deposition of a film of reaction product from a solution containing silicate, chromate, and phosphate ions. Such a layer prevents the formation of hydroxide in boiling water for many hours, and during that period the attack on pure aluminum is negligible.

The passivation process comprises two steps. The first is a 1- to 3-minute immersion at 95° to 100°C in a stripping solution containing 35 cc H₃PO₄ and 20 grams CrO₃ per liter of water. This treatment removes any oxide or hydroxide initially present and is reported⁽³⁾ to deposit a layer about 10Å to 20Å thick containing some phosphate and some Cr³⁺. The second step is an immersion for about 3 minutes at 100°C in a solution containing 10⁻³ M/l each of Na₂SiO₃, CrO₃, and NaH₂PO₄ at a pH of 5.0 ± 0.1. A water rinse completes the treatment. We refer to this sequence of steps as the "SCP treatment." Many variations of time, temperature, and solution composition have been tried in an effort to optimize the protection afforded by the treatment. Such tests have shown that stripping for more than 3 minutes is not beneficial; that all three constituents are necessary in the second bath; that the pH of the second bath is critical; and that increased concentration, especially of silica, in the second bath is harmful.

In order to test the efficiency of the coating, SCP-treated specimens of pure aluminum films prepared by evaporation onto glass were exposed to boiling water in fused SiO₂ beakers. After 17 hours there was no detectable weight change (limit about 2 × 10⁻⁶ g/cm²), and no evidence of hydroxide in the infrared spectrum. A plain aluminum specimen gains

at least 200 × 10⁻⁶ g/cm² in 17 hours, and shows a very strong OH absorption in the infrared. Not only was there no reaction observed on the treated surface, but scratches produced with a diamond scribe after treatment were also inert. Evidently the coating produced by the SCP treatment either has some ductility or has the ability to spread to a certain extent to cover bare areas.

If pseudoboehmite contacts the SCP-treated surface, either because the boiling water test is conducted in an aluminum vessel or because of deliberate seeding, then the surface reacts slowly to form AlOOH and is not as inert. However, even under such conditions the development of the AlOOH layer requires many hours and the reaction is far slower than on an untreated surface.

A few tests of some aluminum alloys (6061, 3002, and 5557) demonstrated that this SCP treatment is effective on alloys as well as on pure aluminum. In one test of 6061 alloy no hydroxide formed in 5 hours in boiling water, although after 18 hours the specimen was covered with hydroxide. Qualitative tests with alloys 3002 and 5557 given the SCP treatment and exposed 24 hours in 1% CuSO₄ or 3 1/2% NaCl solutions at 25°C showed that the SCP-treated specimens had many fewer copper deposits or pits, respectively, compared to untreated specimens.

DISCUSSION

It is interesting that the stripping solution attacks the oxides and hydroxide layers formed on aluminum readily but does not attack the metal. We presume that the reason for this difference is that, as the acid mixture dissolves the natural oxide film on aluminum, eventually a thickness is reached at which electrons can penetrate the film by tunneling. At that time chromate ions are probably reduced to form a layer of a trivalent chromium compound, perhaps a mixed oxide and phosphate, on the surface. This chromium-containing surface layer dissolves only very slowly in the acid, and reaches a thickness at which its growth by electron tunneling balances its dissolution. On a thick anodic oxide no reduction would take place, and the anodic film simply dissolves.

Evidence in support of this mechanism was obtained from potentiostatic experiments. As the potential of an aluminum specimen in the stripping solution is made more positive from the corrosion potential the current rises very rapidly. At a potential only +0.15 volt from the corrosion potential the current was about 5 ma/cm², which corresponds to just the rate at which the stripping solution attacks an anodic film. The addition of a few angstrom units of oxide would reduce the tunneling probability drastically and the Cr³⁺ containing layer would be

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removed, giving a high corrosion rate.

We suppose that the second bath adds some silica to the layer and possibly repairs some thin spots. However, we have no evidence to support these suggestions. The second bath performs some essential function, however, for a specimen exposed only to the stripping bath begins to react after about 10 minutes in boiling water.

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